Time-Resolved Infrared Kinetic Spectroscopy of HO_2, RO_2 and HOONO

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Time-resolved infrared methods can provide important information on the rates and mechanisms of atmospheric reactions involving transient species such as peroxy radicals and short-lived intermediates. We have recently implemented two such methods in our laboratories: near-IR FM kinetic spectroscopy (IRKS) and mid-IR cavity ringdown spectroscopy (IR-CRDS). The former technique has been used as a high-sensitivity probe for HO_2 radicals to study reactions such as $HO_2 + HO_2 \rightarrow$ products, $CH_3O_2 + CH_3O_2 \rightarrow$ products and $HO_2 + CH_3O_2 \rightarrow$ products. While these reactions have been studied several times previously, the high sensitivity of the IRKS method has provided new insights into their rates and mechanisms. The implications of the results for the atmospheric formation of H_2O_2 will also be discussed.

The IR-CRDS technique has been employed to study the reactions

$$OH + NO_2 + M \rightarrow HONO_2 + M$$
$$\rightarrow HOONO + M$$

Gas-phase infrared spectra of HOONO have been obtained for the first time in the region of the OH fundamental, and branching ratios for the two product channels have been obtained as a function of temperature. These results will be compared with predictions based on the kinetics of OH disappearance at high pressure.